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SUPERLATTICES GROWN BY OMVPE

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Superlattices of InGaAs/InP have been grown by OMVPE using short interval H₂-only growth interrupts to eliminate intermixing of hydride gases at the heterojunction interfaces. Changes in lattice strain resulting from interlayer alloying were measured by X-ray diffraction. The changes in strain are small and consistent with decomposition of the surfaces when exposed to the nonequilibrium H₂ vapor. Possible interface smoothing is seen with H₂ interrupt at the InGaAs to InP transition. A large compressive strain contribution is unaffected by the interrupts and is attributed to As carryover into the InP from surrounding solid deposits rather than the transport gases.

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Effects of hydrogen-only interrupts on InGaAs/InP superlattices grown by OMVPE

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Superlattices of InGaAs/InP have been grown by OMVPE using short interval H₂-only growth interrupts to eliminate intermixing of hydride gases at the heterojunction interfaces. Changes in lattice strain resulting from interlayer alloying were measured by X-ray diffraction. The changes in strain are small and consistent with decomposition of the surfaces when exposed to the nonequilibrium H₂ vapor. Possible interface smoothing is seen with H₂ interrupt at the InGaAs to InP transition. A large compressive strain contribution is unaffected by the interrupts and is attributed to As carryover into the InP from surrounding solid deposits rather than the transport gases.

1. Introduction

Interface abruptness in InGaAs/InP multiple layer structures is a concern for OMVPE growers who fabricate epilayer configurations for device development. Application of the heterojunctions to quantum sized geometries demands epilayer material that closely approaches the ideal monolayer-abrupt transition from one semiconductor composition to the other on which modeling of the electronic structure is based. The perfect interface is not easily achieved, although quite satisfactory quantum well superlattices and other structures can be produced with good control of composition and thickness uniformity necessary for tailoring optical and electronic characteristics. Many of the studies of thin single quantum wells demonstrate flat interfaces whose photoluminescence spectra show discrete, separate peaks attributed to abrupt, monolayer variations of the well thickness [1,2]. However, photoluminescence data do not explicitly show the interface to occur between intended compositions of InP and In_{0.53}Ga_{0.47}As. Some compositional intermixing

may exist which is not obvious from photoluminescence measurements, but does affect the band offsets of the heterojunctions [3].

The accumulated thickness of many identical superlattice periods rather than just a single quantum well provides opportunity for characterization techniques such as high resolution X-ray diffraction and infrared absorption. One result of X-ray lattice parameter studies in the InGaAs/InP superlattices we have grown, as well as those reported by others for both OMVPE [4] and GSMBE [5], is the occurrence of a compressive strain when using a gas composition which normally provides lattice-matched thick (> 1 μm) In_{0.53}Ga_{0.47}As layers. In practice we achieve lattice-matched superlattices by adjusting the composition slightly Ga-rich, presuming that the tensile stress of the mismatched InGaAs balances a compressive stress associated with the interfaces.

Vandenberg et al. [6] suggest that some stress is intrinsic due to different atomic bond lengths for As and P at the interface. There can also be stress from compositional intermixing across the interface. For example, As in InP forms compressive

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sively stressed InAsP and P in lattice matched InGaAs from a tensilely stressed InGaAsP. On the just grown layer this type of alloying occurs from exposure of its surface to the hydride of the next layer. Exposure of InP to arsine and InGaAs to phosphine causes surface substitution of the group V components [7]. Similarly, on the to be grown side of the interface, carryover of the previous group V as vapor will contaminate the subsequent growth. With OMVPE some intermixing is very likely to occur due to gas exchange during the heterojunction growth, thus the strain may be influenced by changes of growth technique such as use of interrupts. For most interrupt studies the solid has been exposed to arsine, phosphine or combinations thereof [1,4,8,9] which are likely to form mismatched alloys. Interrupts without hydride have also been used [10]; however, extended absence of the hydride overpressure results in loss of the volatile group V constituent from the layer surface. It is not easy to identify directly which strain mechanism is occurring at which interface, and we must infer the effect of changes in OMVPE gas switching technique from the finished superlattice.

In this investigation we have studied changes in lattice strain due to the use of brief growth interrupts with the absence of all source gases at the layer transitions. The intention is to purge the chamber of source gas before starting the next layer while minimizing the time for surface loss of volatile As or P. The InGaAs grown on InP interface (interface 1), and the InP grown on InGaAs interface (interface 2) were studied separately.

2. Experimental procedure

The OMVPE growth was performed on InP (100) substrates at 650°C and 20 Torr from trimethylindium (TMIn), trimethylgallium (TMGa), arsine and phosphine in a 44 mm diameter cross-section horizontal quartz reactor using a lamp heated, 25 mm W × 65 mm L, 8° taper, graphite susceptor. Vent/run gas switching was achieved using a Thomas Swann Epifold with the vent/run pressures carefully balanced and con-

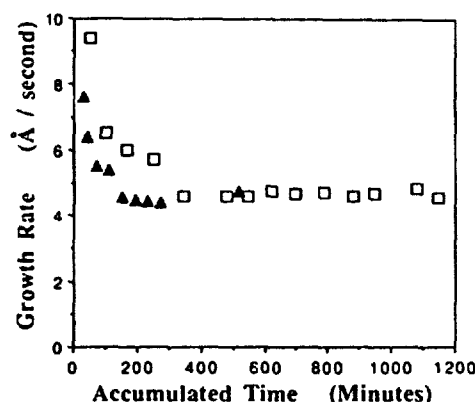


Fig. 1. The change of OMVPE growth rate as a clean quartz chamber accumulates sidewall deposits. Set 1 (□) up to 350 min was InP growth, with subsequent growth being a mix of InP and InGaAs/InP superlattices. The set 2 (●) growths were InGaAs and InGaAs/InP superlattices.

stant gas flow maintained by adding hydrogen in the absence of source gas flow. A total gas flow of 1.5 l/min provides a gas velocity at 20 Torr chamber pressure of ~ 1 m/s to ensure rapid gas displacement. To adjust for day-to-day composition and growth rate variations resulting from TMI vapor pressure drift and drift of the mass flow controller electronics, a daily calibration growth of a superlattice with no interrupts was performed as a reference to normalize the measured strain. Establishing conditions for good reproducibility to allow monitoring small changes in strain was not trivial. Reproducible growth conditions could be achieved only when sidewall deposits in the chamber had built up to provide an unvarying partition of source depletion between the substrate and its surroundings. Fig. 1 demonstrates that growth rates in a clean tube are much higher than for a tube conditioned by previous growths. These data are from mixed sequences of InP, InGaAs and InGaAs/InP superlattices. The thick layer growth rates were from gravimetrically determined thicknesses and the superlattice rates from X-ray superlattice period spacings. There are evident differences in the chamber conditioning time required for a growth rate equilibrium. The set 1 data for accumulated growth time of less than 350 min were for only InP growths which show a gradual decrease in growth rate corresponding to a slow build-up of sidewall de-

posits. When arsine is used, the deposits build up much faster, as seen for the InGaAs and superlattice growths of set 2. The growth interrupt studies were performed only in the constant growth rate regime to achieve reproducibility for comparing small changes in lattice strain.

Another constraint to achieving reproducible lattice-matched superlattices is memory of previously grown material. The sidewall and susceptor solid deposits necessary for uniform growth rates are also a reservoir for volatile group V source carryover. This is particularly evident for As following InGaAs growth. Fig. 2 shows the SIMS composition profile of an InP region containing three thin InGaAs marker layers that was grown on a thick InGaAs layer on an InP (100) substrate. The resolution is not adequate to assess composition mixing at the interfaces; however, residual levels of P in InGaAs and of As in InP are evident. Of particular significance is the prolonged carryover of As into the InP following the thick InGaAs growth. One consequence of this behavior is that superlattices grown immediately following thick InGaAs growth show larger compressive mismatch from increased As levels in InP; thus care was taken that growths for comparison of strain were in a chamber with a predominantly InP growth history. The only InGaAs

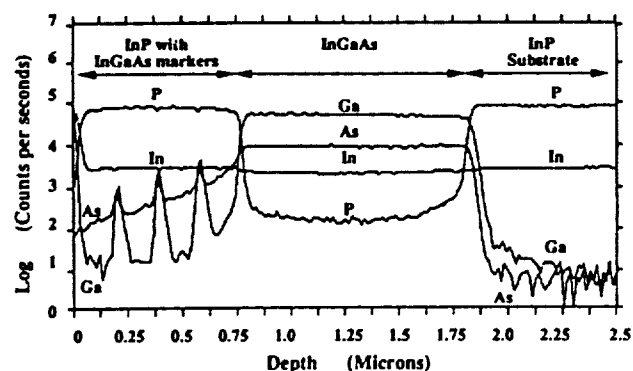


Fig. 2. SIMS profile of an InP thick layer with InGaAs markers (of intended thicknesses 3, 10, and 20 Å from left to right) which was grown after a thick InGaAs layer, showing a large carryover of As into the InP. The SIMS data were taken with a Perkin-Elmer 6300, using a Cs beam at 7 kV. The sample was tilted at 45°, and the raster area was 700 μm^2 (gated 80%), resulting in a beam current of 250 nA. Ions monitored were $^{113}\text{In}^+$, $^{69}\text{Ga}^+$, $^{75}\text{As}^-$ and $^{31}\text{P}^-$.

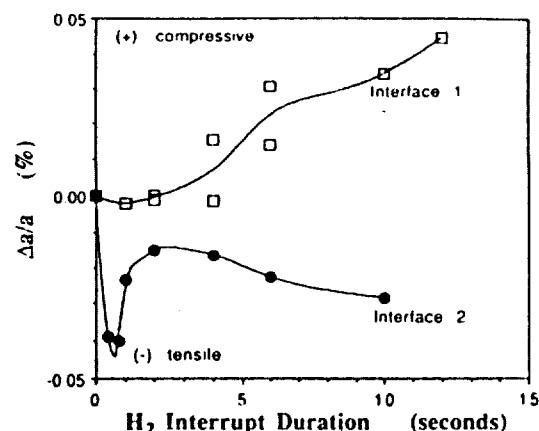


Fig. 3. Change of strain in a 30 period, InGaAs (70 Å)/InP (140 Å) superlattice with (1) H_2 -only interrupt at the InGaAs grown on InP interface (\square) and (2) H_2 -only interrupt at the InP grown on InGaAs interface (\bullet).

growth was limited to the quantum wells, and each superlattice was grown on a 2500 Å InP buffer layer.

Growths under identical conditions were performed with interrupts independently introduced at interface 1 and at interface 2 using the basic superlattice structure of 30 periods of a 70 Å InGaAs well and a 140 Å InP barrier. Composition of the InGaAs was fixed to provide a lattice-matched superlattice when no interrupts were used. Shifts of the strain determined from high resolution (400) X-ray rocking curves were used to describe the effect of growth interrupts. The relaxed strain was calculated from the vertical lattice spacing corrected by the Poisson ratio [11].

The effects of H_2 interrupts on the strain are shown in fig. 3. For interface 1 there is negligible change of strain for intervals less than 2 s, and for longer interrupts there is a time proportional increase in compressive strain. Two seconds is longer than the time expected to allow complete purge of phosphine before starting the InGaAs growth, thus the absence of any significant change suggests there must already be an abrupt transition from InP to InGaAs growth without interrupts. The growth rate is ~ 4 Å/s so it is feasible that uninterrupted gas exchange is complete within growth of one 3 Å monolayer. For longer interrupt intervals we expect generation of surface vacancies by P dissociation to the nonequi-

librium H_2 atmosphere, and these vacancies will subsequently fill with As to form a compressively strained InAsP consistent with the observed results.

The effects of interrupts on interface 2 in fig. 3 show two features to the strain. First is a sharp initial increase in tensile strain followed by a drop. This behavior at short intervals is superimposed on a slow monotonic increase in tensile strain with interrupt duration. The slow increase is expected from generation of As vacancies in the InGaAs which are subsequently filled with P upon start of the InP growth. The behavior for times less than 2 s may be related to smoothing of a rough InGaAs surface. An initially rough surface would allow more rapid exchange of P for As. After smoothing takes place, the newly established two-dimensional surface would have less sites available for the As-P exchange with the longer interrupts and would show the slower monotonic increase of strain.

Assessment of growth with H_2 -only interrupts on the room temperature infrared absorption spectra shows virtually no effect. The exciton absorption peak wavelength and half-width of half-maximum were not changed.

Possible group III compositional transients at the start and stop of InGaAs growth were studied by growing thick layers composed of periodic segments separated by interrupts. Pseudosuperlattices of 71 periods of 70 Å InGaAs with 2 s interrupts under both AsH_3 and H_2 -only were grown. Neither SIMS nor X-ray diffraction show evidence of a periodic compositional transient, and room temperature infrared absorption spectra are indistinguishable from continuously grown InGaAs. Hall mobilities of the interrupted InGaAs were consistently higher which could result from either compositional ordering or reduced impurity incorporation. However, no obvious group III redistribution was observed within the limits of our analysis.

3. Discussion and conclusions

Short interval H_2 -only interrupts in low pressure OMVPE growth of InGaAs/InP superlat-

tices show remarkably little effect on compositional alloying at the interfaces. Resulting changes in the lattice strain in fig. 3 are only a small fraction of the strain which is associated with the interfaces based on the Ga-rich $In_xGa_{1-x}As$ composition used to achieve lattice-match. The composition was $x = 0.485$ based on the settings of In and Ga gas flows, and this would give a relaxed lattice mismatch of $\Delta a/a = -0.32\%$. The dominant cause of the strain is thus little changed by the purge of the source gases between layers. The use of H_2 interrupt intervals of about 2 s at each interface gives assurance of minimal intermixing of the hydride gases with no evident detriment to the interfaces. The possibility of surface smoothing at interface 2 suggests a definite advantage to using an interrupt and is worthy of further study. Otherwise the use of H_2 interrupts is of no great advantage.

The small dependence of strain on H_2 interrupts indicates the dominance of some growth parameter other than the gas switching in causing the compressive strain in these superlattices. As-carryover as seen in the thick layer SIMS profile has also been observed by others [12-14], and it is likely that this is the dominant contribution to superlattice mismatch. As-carryover is consistent with the results of this study provided the source of As is not the arsine which we can control with the interrupts, but is from As evolved from heated deposits on the susceptor and sidewalls. Bhat et al. [7] have demonstrated the effectiveness of physical vapor species As_4 and P_4 from adjacent wafers of GaAs or InP in providing a protective atmosphere for preserving structured layer surfaces during heating for OMVPE growth. The exposed solid deposits in our reactor very likely serve as a similar source of As_4 and P_4 . The presence of a group V partial pressure would explain the relatively small surface dissociation during H_2 -only interrupts. However, Stringfellow [15] points out that incorporation of the very stable tetramer is not favorable, thus may not itself be a candidate for carryover contamination. Nevertheless, interaction of the pyrolyzed gases in equilibrium with the solid deposits could release an active form of the contaminant. The favored incorporation of As enhances the carry

over contamination of InP compared to P contamination of InGaAs, thus one expects a compressive strain associated with interface 2 to dominate.

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